Local and electronic structure around manganese in $Cd_{0.98}Mn_{0.02}Te_{0.97}Se_{0.03}$ studied by XAFS

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Local and electronic structure around manganese in $Cd_{0.98}Mn_{0.02}Te_{0.97}Se_{0.03}$ studied by XAFS

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Abstract. X–ray Absorption Fine Structure (XAFS) technique was employed to study local electronic and structural features of Mn ions incorporated in $Cd_{0.98}Mn_{0.02}Te_{0.97}Se_{0.03}$. XAFS measurements performed at Mn K edge revealed that manganese Mn(II) ions are well incorporated into the host CdTe lattice (cubic zinc–blende structure type) and their immediate surrounding is found to be composed exclusively of Te atoms. The observed preference of Mn ions distribution around Te opposes earlier observations on the similar systems, where preferential Mn–Se over Mn–Te paring was found.

1. Introduction

II–VI semiconductors doped with transition metals, known as diluted magnetic semiconductors (DMS), are of scientific interest because of their wide range of optical, magnetic and electronic transport properties. The ternary nature of DMS allows for tuning the band gap and the lattice constant by varying the composition of the material, while by changing the concentration of the magnetic species the magnetic and magneto–optical properties can be altered. In quaternary systems [1–4] the possibilities to tune the material properties are even more extended owing to the additional degree of freedom an extra ion component contributes to. Another peculiarity of the later systems is that the ion substitution exhibits the nearest–neighbour and site occupation preferences (SOPs) in both cation and the anion sub–lattices [2–4].

This paper focuses on the X–ray Absorption Fine Structure (XAFS) studies of $Cd_{1-x}Mn_xTe_{1-y}Se_y$ (x=0.02, y=0.03). Low concentrations x and y ensure that the trahedrally coordinated zinc–blende (ZB) type structure of the host CdTe is preserved. To gain precise information on local and electronic structure, valence, and short range order of the immediate surrounding of manganese atoms, both X–ray Absorption Near Edge Structure (XANES) and Extended X–ray Absorption Fine Structure (EXAFS) were employed and the results of the preliminary analysis are presented.

2. Experimental

XAFS (XANES/EXAFS) measurements were performed on $Cd_{0.98}Mn_{0.02}Te_{0.97}Se_{0.03}$ single crystals grown by the Bridgman method. Details on the sample's preparation are given in [5]. Manganese K edge data were collected in fluorescence mode at 77 K and 293 K on the HASYLAB A1 Beamline at Deutsches Elektronen–Synchrotron DESY (Hamburg, Germany). The synchrotron radiation source was operating at electron beam energy of 4.45 GeV with the maximum stored current 120 mA. The

A1 station uses double crystal monochromator with two Si–(111) crystal pairs. Samples were oriented at 45° to the incident beam direction and a 7–cell SDD detector was used to collect the spectra. XAFS data processing and analysis were performed using IFEFFIT [6] as implemented in ATHENA and ARTEMIS software packages [7]. The interatomic distances (r), mean–square variation of the distances (σ^2) and the edge shift correction (E_0) were treated as free parameters during the fitting procedure. The passive electron reduction factor S_0^2 was determined from the procedure described in [8]. The obtained value S_0^2=0.63 (see Figure 1) was then kept fixed throughout the analysis.

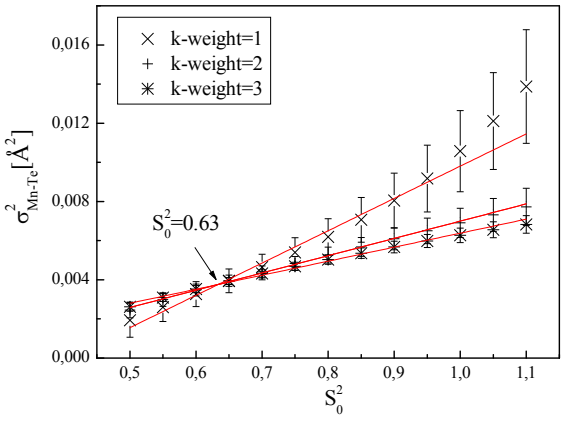

Figure 1. Parameter S_0^2 for the Mn K–edge in $Cd_{0.98}Mn_{0.02}Te_{0.97}Se_{0.03}$, as determined from the first shell fits successively performed with different k–weights (1, 2 and 3) and the values of S_0^2 fixed from 0.5 to 1.1, with step 0.05.

3. Results and discussion

The k–weighted Mn K edge EXAFS spectra of $Cd_{0.98}Mn_{0.02}Te_{0.97}Se_{0.03}$ taken at T=77 K and T=293 K are presented in Figure 2. The corresponding Fourier transformed spectra with their best fits are presented in Figure 3. The results are summarized in Table 1.

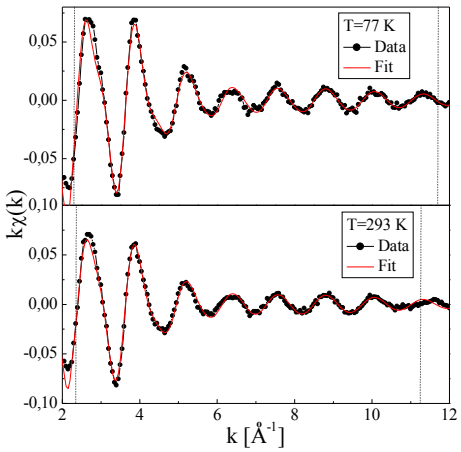

Figure 2. The k–weighted EXAFS function $k\chi(k)$ extracted from the Mn K edge absorption data at T=77 K (upper part) and at T=293 K (lower part), with the vertical lines denoting the k–ranges over which Fourier transforms (FT) of the data (represented with points) were taken and analyzed. The best fits are represented with lines.

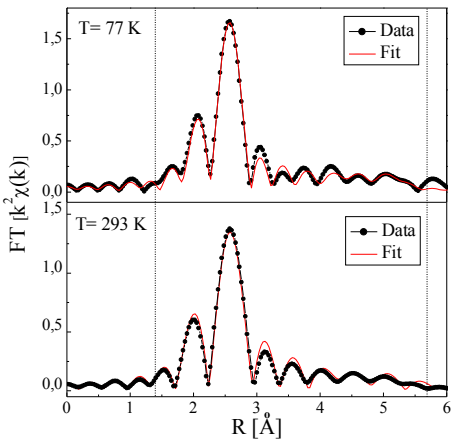

Figure 3. Fourier transforms (FT) of the k^2–weighted EXAFS function $k^2\chi(k)$ extracted from the Mn K edge absorption data at T=77 K (upper part) and at T=293 K (lower part), with the vertical lines denoting the fitting ranges. The experimental data are represented with points and the best fits with lines.

According to these preliminary results, in the investigated sample manganese is surrounded by four equidistant tellurium atoms. Selenium atoms were not found in the immediate environment of Mn,

which disagrees with previously observed preferences for Mn–Se paring [2]. The Mn–Te bond length (2.866–2.867 Å, see Table 1) is longer than in ZB form of MnTe (2.75 Å) and approaches the value in NiAs–type MnTe (2.93 Å). This agrees with the theoretical predictions that in CdTe–based alloys the Mn–Te bond length should stay nearly constant around the value in NiAs–type MnTe [9], but opposes the experimental observations, according to which the local Mn–environment stabilizes in ZB–type MnTe [3]. Interatomic distances involving second and third coordinations are within experimental uncertainties the same as in host CdTe (4.58 Å and 5.37 Å, respectively), which confirms the dominance of nearest neighbour interactions in the alloy [3]. In the investigated temperature range (77– 293 K) the obtained interatomic distances of all three coordination shells around Mn are only slightly temperature dependent.

Table 1. Structural parameters as obtained from the Mn K edge EXAFS data analysis: *r*–interatomic distance, σ^2–mean–square variation of the distance between Mn atom and atoms in the surrounding coordination shells, *n*–coordination number, E_0–the edge shift correction and the fit quality factor R.

	T=77 K			T=293 K		
	Mn–Te(1)	Mn–Cd	Mn–Te(2)	Mn–Te(1)	Mn–Cd	Mn–Te(2)
r [Å]	2.866(3)	4.55(4)	5.44(4)	2.867(4)	4.55(6)	5.44(7)
σ^2 [Å^2]	0.0037(2)	0.030(7)	0.024(6)	0.0040(4)	0.037(1)	0.036(2)
n	4	12	12	4	12	12
E_0 [eV]	0.9(4)			0.8(5)		
R–factor	0.020			0.026		

XANES spectrum taken at the Mn K edge at T=77 K is presented in Figure 4 a. The spectrum taken at T=293 K is identical in shape and therefore it was not shown. The pre edge arises from the electronic transitions into the lowest unoccupied states partially formed by empty Mn 3d–states, and contains valuable information about the local symmetry, valence state and degree of hybridisation with Te 5p states. The pre edge (see inset of Figure 4 a) was fitted with a Lorentzian function and an arctangent function is used to approximate the baseline. The normalized pre–edge peaks at the two temperatures are symmetric in shape and their energy position meet at E=6540.5 eV (see Figure 4 b) which corresponds to Mn in 2+ valence state (Mn(II)) [10]. Slightly longer Mn–Te distance at T=293 K yields somewhat lower degree of pd–hybridisation and therefore the intensity of the pre–egde peak is a little lower (see Figure 4 b).

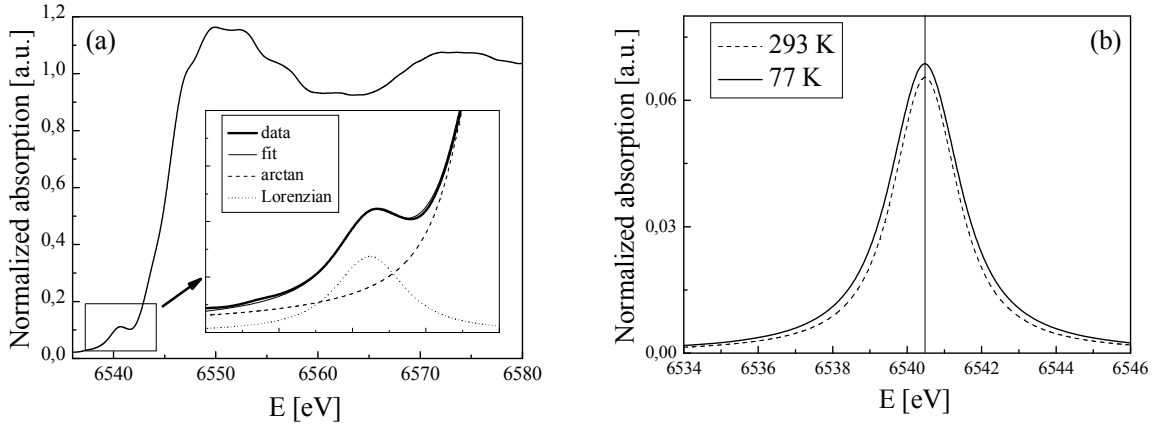

Figure 4. (a) The Mn K–edge XANES spectrum with the normalization of the pre–edge region shown in inset; (b) the pre–edge region normalized.

4. Conclusion

In conclusion, X–ray Absorption Fine Structure (XAFS) technique was employed to study local electronic and structural features of Mn ions incorporated in $Cd_{0.98}Mn_{0.02}Te_{0.97}Se_{0.03}$. Manganese Mn(II) ions are found to be well incorporated into the host CdTe lattice in symmetric local environment composed of four equidistant Te atoms, with the Mn–Te bond length approaching the value in NiAs–type MnTe. The second and third coordination shell atoms seem not to be affected by the Mn presence and stay close to their ideal positions in host CdTe.

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